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Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study

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ABSTRACT

Thermochemical properties of 1,3-propanediol are in disarray. A new standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation at the temperature $T = 298.15$ K of the liquid 1,3-propanediol was measured using combustion calorimetry. A new molar enthalpy of vaporisation of 1,3-propanediol was derived from the vapour pressure temperature dependence measured by the transpiration method. Thermodynamic data on 1,3-propanediol available in the literature were collected, evaluated, and combined with own experimental results. This collection together with the new experimental results reported here has helped to resolve contradictions in the available enthalpies of formation data and to recommend the set of vaporisation and formation enthalpies for 1,3-propanediol at $T = 298.15$ K (in kJ · mol^{-1}): $\Delta_f H^\circ_m$ (g) = −(410.6 ± 2.2), $\Delta_f H^\circ_m$ (l) = −(481.8 ± 2.2), and $\Delta^g_l H^\circ_m = (71.2 \pm 0.2)$ as the reliable benchmark properties for further thermochemical calculations. Quantum-chemical calculations of the gas phase molar enthalpy of formation of 1,3-propanediol have been performed using the G3MP2 method and results were in excellent agreement with the recommended experimental values. The standard molar entropy of formation and the standard molar Gibbs function of formation have been calculated.

1. Introduction

The manufacturing of renewably-sourced platform chemicals and polymers is an active area of interest [1]. Large scale fermentation of glycerol [2] or glucose [3] to form 1,3-propanediol is an attractive way for valorisation of renewable feed stocks since 1,3-propanediol is a valuable precursor for production high value polymers and intermediates [3]. New strategies to utilise renewable feedstock into value-added products are important for the future competitiveness of the chemical industry. Chemical feasibility of new strategies has to be assessed using thermodynamic calculations. Reliability of the prediction is crucially dependent on the quality of experimental data involved in the calculations. Surprisingly, the available thermochemical values for alkanediols are in disarray [4]. The standard molar enthalpy of formation, $\Delta_f H^\circ_m$, of 1,3-propanediol in the liquid state reported in the literature [5–7] from combustion calorimetry measurements show spread over 15 kJ · mol^{-1}. New additional experiments with 1,3-propanediol are intending to resolve contradictions among available data. This contribution complements and extends our previous work on thermodynamics of aliphatic diols by our group [4,8,9]. The aim of this study is an experimental and computational study of 1,3-propanediol in order to evaluate available thermochemical properties.

2. Materials and methods

2.1. Materials

A sample of 1,3-propanediol available from Alfa Aesar with mass fraction purity 0.99 was further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.02 mass percent) could be detected in the samples used for the combustion experiments and the vapour pressure measurements. The degree of purity was determined using a GC with capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 K · s^{-1} to $T = 523$ K. Provenance and purity of the compound prepared for thermochemical studies in this work are given in table S1 (Supplementary information).

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